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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improved Adhesive Compositions

We, UNION CARBIDE CORPORATION, a Corporation organized under the Laws of the State of New York, United States of America, of 270, Park Avenue, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improved adhesive compositions. More particularly the present invention relates to chloroprene polymer adhesive compositions exhibiting improved bonding characteristics.

Various adhesive compositions based upon chloroprene polymers have been proposed in the past. These compositions have generally exhibited excellent adhesion for short periods of time. However, as coatings of these adhesive compositions age in the air, the adhesive properties of the surface rapidly diminish. This short range of tack necessitates the immediate use of the adhesive after it has been applied to a substrate and exposed to air.

Until the present time, no chloroprene polymer base adhesive composition had been proposed which exhibited a high degree of adhesion coupled with a completely effective long tack range.

In accordance with the present invention improved adhesive compositions have been discovered which exhibit a high degree of adhesion for long periods of time after application. These adhesive compositions comprise a chloroprene polymer as hereinafter defined, a rosin ester of a terpene-phenol condensate, an oxide of a polyvalent metal, and a solvent for said chloroprene rubber.

Chloroprene polymers are elastomeric

materials formed by the polymerization of chlorobutadiene. By the term "chloroprene polymers" is meant copolymers of chloroprene and other polymerizable monomers such as styrene, isoprene, acrylonitrile and the like wherein chloroprene represents the predominant monomer polymerized, as well as chloroprene homopolymers. Generically these elastomers are known as neoprene rubbers. While any of the chloroprene elastomers can be used in the compositions of the present invention, homopolymers are preferred and those polymers having relatively rapid rates of crystallization after milling are especially preferred. These preferences are dictated by the enhanced adhesive properties exhibited by compositions utilizing such polymers.

The rosin esterified terpene-phenol condensates which are used in the compositions of the present invention are those formed from the esterification of terpene-phenol condensates with rosin in the presence of an acid catalyst. The preparation of these esterified condensates is described in U.S. Patent 2,284,156 to Lemmer et al. issued May 26, 1942. Generally, the preparation of these resins comprises condensing a terpene and a phenol in a ratio of from 1:1 to 1:10 parts by weight terpene to phenol respectively. The condensation is generally accomplished by heating the terpene-phenol mixture to a temperature of from 0° C. to 150° C. in the presence of a strong catalyst such as sulfuric acid, sulfonic acid, aluminum chloride, boron trifluoride complexes, oxalic acid-boric acid mixtures and the like.

The terpene-phenol condensate is then esterified with rosin by heating the condensate mixture and from 1 to 4 parts rosin at a temperature of from about 260° to about 280° C. in the presence of an acid or basic esterification catalyst such as boric acid, sul-

— chloroprene
— terpene-phenol condensate/rosin ester
— metal oxide

furic acid, sodium hydroxide or the like. The reaction period is generally from 3 to 20 hours. The esterified condensate can be recovered as residue by distillation of the reaction mixture or by other conventional means.

5 The phenols which can be used to form condensates include phenols having at least one active ortho or para position on the benzene ring. For the purpose of the present invention such phenols will be defined as "active" phenols. Illustrative of active phenols are hydroxybenzene, cresol, xylene, chlorophenol, dichlorophenol, nitrophenol, catechol, resorcinol, hydroquinone, bis(*p*-hydroxyphenyl)methane, bis(*p*-hydroxyphenyl)ethane, 2,2 - bis(*p* - hydroxyphenyl)propane, and the like.

10 Terpenes which will form useful condensates with the active phenols are the terpene hydrocarbons having the general formula $C_{10}H_{16}$ such as α -pinene, β -pinene, dipentene, terpinene, limonene, 7-methyl - 3 - methylene-1,6-octadiene, and the like and terpene alcohols such as terpenolene and the like.

25 Rosins which will esterify the terpene-phenol condensates include gum rosin wood rosin and tall oil rosin all of which are well known in the art. These rosins contain large amounts of rosin acids in mixture which in fact esterify the condensate. It has been found that the tall oil rosins produce condensate esters having particularly desirable properties and are therefore preferred.

30 The rosin ester of a terpene-phenol condensate which is preferably used in the compositions of the present invention is the tall oil rosin ester of the α -pinene condensate of phenol.

40 The rosin esterified terpene phenol condensates are preferably used in the compositions of the present invention in amounts of from 5 to 200 parts by weight per 100 parts chloroprene polymer and are usually used in amounts of from 25 parts to 75 parts by weight per hundred parts chloroprene polymer.

45 Solvents which are suitable in the compositions of the present invention are those which will dissolve chloroprene polymer. Such solvents include the aromatic hydrocarbon solvents such as benzene, toluene, xylene and the like aliphatic ketones such as acetone, methylethyl ketone, methylisobutyl ketone and the like, the chlorinated aliphatic hydrocarbons such as trichloroethylene, and lower aliphatic esters such as ethyl acetate, amyl acetate and the like. While aliphatic hydrocarbons are not suitable solvents, they may be used in equal amounts or less with the aforementioned solvents as diluents. Additionally, mixtures of the aforementioned solvents can be used.

60 The amount of solvent used in the present

compositions is determined generally by the use to which adhesive composition is to be put and is therefore not limited to a specific amount. However a sufficient amount of solvent should be used to facilitate application of the composition in its intended use. Generally from about 250 to 400 parts of solvent per hundred parts of chloroprene polymer will suffice.

70 By the term "Polyvalent metal oxides" is meant the oxides of those metals which exhibit a valence greater than 1. Preferred in the compositions of this invention are the polyvalent metal oxides of Group II metals of the Periodic Chart of the Elements as found in "The Merck Index" inside cover 7th edition, 1960, published by Merck and Co., Inc. Illustrative of the polyvalent metal oxide of group II are magnesium oxide, zinc oxide, calcium oxide, barium oxide, and the like. Especially preferred polyvalent metal oxides are magnesium oxide, zinc oxide and mixtures thereof because these oxides are non-toxic, low in density, and readily available.

85 The polyvalent metal oxides are generally used in an amount of from 1 to 32 parts by weight per hundred parts by weight chloroprene polymer.

90 Antioxidants can be used in the present compositions although they are not essential ingredients. Suitable antioxidants include compounds such as di-*t*-butyl-*p*-cresol, phenyl- α -naphthylamine and phenyl- β -naphthylamine. When antioxidants are used in these compositions they are used in amounts of from 1 to 2 parts by weight per hundred parts by weight neoprene.

100 If desired, other ingredients such as fillers, pigments, thickening agents and the like can be added to the present compositions to reduce the cost, color, or modify the viscosity of the compositions.

105 It has additionally been found that maleic or fumaric acid or maleic anhydride will add to rosin and that the presence of this addition product increases the peel strength of the adhesive compositions of this invention. If these addition products are used, it is desired to form them in situ in the terpene-phenol condensate esterification reaction as the acids will add rosin under these conditions and only one reaction is required. These acid or acid anhydride additives are used in amounts of from 0 to 32 parts by weight per hundred parts rosin used.

Evaluation Procedure

120 The various esterified terpene-phenol condensates prepared in preparations 1-6 below, were evaluated as follows:

Each resin was incorporated in a typical adhesive composition as follows:

Chloroprene homopolymer Neoprene AC

100 parts by weight

Manufactured by DuPont DeNemours Co. stabilized with thiuram disulfide

Zinc oxide	5
Magnesium Oxide	4
Antioxidant di- <i>t</i> -butyl- <i>p</i> -cresol	1
Rosin Esterified Terpene phenol Condensate	45
Toluene	335

The chloroprene homopolymer zinc oxide, magnesium oxide, and antioxidant were compounded on a two roll mill. This mixture was then dissolved in 290 parts of toluene. The rosin esterified terpene-phenol condensate was dissolved in 45 parts of toluene. The resin and neoprene solutions were then mixed together to form the finished adhesive.

10 *Peel Strength Test*

Canvas to Canvas

Two strips of 10.1 ounce 54×42 weave army duck canvas 8 inches by 1.5 inches were each given two coats of adhesive with a brush. The first coat was allowed to dry about one hour before the second coat was applied. The coated strips were placed in contact and pressed together with a ten pound roller. The edges of the specimens were cut off to give a one inch strip. Testing was conducted in a tensile machine at a rate of one inch per minute with tests being run one, two, and three weeks after assembly.

25 *Peel Strength Test*

Canvas to Steel

A 1.5 inch by 12 inch strip of canvas was adhered to a 3 inch by 6 inch cold rolled steel panel which had been cleaned by wiping with acetone and toluene. The canvas was given two coats of adhesive as in the canvas to canvas peel strength test, and the steel coat was given one coat at the same time the second coat was applied to the canvas. Assembly and testing was the same as described in the canvas to canvas peel strength test.

40 *Tack Range Test*

A film of adhesive was applied to both 50 pound Kraft paper and glass with a 10 mil draw down bar. At frequent intervals 0.5 inch strips of the coated paper were laid film side down on the coated glass and immediately stripped off. The time that elapsed before the coated paper no longer adhered was recorded as the tack range.

EXAMPLE

A. Preparation of Terpene-Phenol Condensate

To a five liter four-necked flask were charged 3040 grams of phenol, 23.2 grams of anhydrous oxalic acid and 5.2 grams of boric acid. The temperature of this mixture was raised to 85° C. Carbon dioxide was passed over the reaction mixture throughout the reaction. When the acids were dissolved, 735 grams of α -pinene were slowly added over a period of 70 minutes. The resulting reaction was exothermic and cooling with a water bath was necessary to maintain the reaction temperature at about 85° C. After the α -pinene addition was complete the reaction mixture was heated to a temperature of 100° C. and maintained at that temperature for a period of one and one half hours. The reaction mixture was then vacuum distilled to a temperature of 214° C. at a pressure of $\frac{1}{2}$ inch of mercury. The resin recovered as residue was light yellow orange in color and had a ring and ball melting point of 188° F.

B. Preparation of Rosin esterified to terpene-phenol condensate

1. Ninety grams of tall oil rosin and 35 grams of the α -pinene-phenol condensate prepared in section A above were charged to a flask and heated to a temperature of 260° C. under three inches of mercury pressure for a period of eleven and one half hours. The rosin ester was recovered directly. The ester was light orange in color, it had a ring and ball melting point of 216° F. and an acid number of 47.

2. Ninety grams of tall oil rosin and 35 grams of α -pinene-phenol condensate prepared in section A above were charged to a flask equipped with a Dean-Stark trap. The reaction mixture was heated to a temperature of 280° C. and xylene was added to the trap in an amount sufficient to maintain the reflux temperature at 280° C. The reaction was maintained at this temperature for a period

- of four and one half hours, after which it was vacuumed distilled to a temperature of 276° C. under one inch of mercury pressure. The esterified condensate was recovered as residue. This condensate was light yellow orange in color and had a melting point of 199° F.
3. In a manner identical with 2 above 90 grams of tall oil rosin, 35 grams of the α -pinene-phenol condensate from A above and 10 grams of maleic anhydride were reacted under the conditions of 2 above for a period of four hours.
- The maleic modified rosin esterified α -pinene-phenol condensate was light orange in color and had a melting point of 247° F.
4. In a manner similar to that described in 2 above ninety grams of tall oil rosin was reacted with 25 grams of α -pinene-phenol condensate prepared in Section A above, at a temperature of 280° C. at a pressure of one inch of mercury for a period of four hours.
- The esterified α -pinene-phenol condensate prepared in Section A above, at a temperature of 280° C. at a pressure of one inch of mercury for a period of four hours. The esterified α -pinene-phenol condensate was recovered directly. This product was light yellow orange in color and had a melting point of 192° F.
5. Preparation 4 above was repeated exactly except that 45 grams of α -pinene-phenol condensate A above was used instead of 25 grams. The rosin esterified α -pinene-phenol condensate had a melting point of 212° F.
6. Preparation 4 above was repeated exactly except that 60 grams of the α -pinene-phenol condensate of A above was used instead of 25 grams. The esterified product had a melting point of 201° F.
- The table below shows the tensile peel strengths and tack ranges for each of the rosin esterified terpene-phenol condensates.

TABLE I

Peel Strength at 73°F.

Tackifying Resin Additive	Days Aged at Room temperature before testing	Canvas to Canvas weeks aged			Canvas to Steel weeks aged			Tack Range
		1	2	3	1	2	3	
*Control 1	2							10 minutes
**Control 2	19	25	27	29	9	9	10	4 minutes
Esterified Condensate 1	19	27	29	35	5	7	11	2 days
Esterified Condensate 3	19	29	35	37	9	15	17	2 days
Esterified Condensate 2	1	19	26	31	4	6	8	6 days
**Control 2	1	17	20	20	3	7	5	7 minutes
Esterified Condensate 4	3	26	30	31	5	6	8	2.5 days
Esterified Condensate 5	3	13	27	26	2	5	8	5 days
Esterified Condensate 6	3	19	30	32	4	8	12	2.5 days
***Maleic anhydride-rosin adduct and Esterified condensate		36	39	38	9	11	14	250 minutes

*Control 1 additive consisted solely of tall oil rosin

**Control 2 additive consisted solely of α -pinene-phenol condensate A

***Ten parts of maleic anhydride, 90 parts of gum rosin and 35 parts of α -pinene-phenol condensate were reacted for 6.5 hours at a temperature of 280°C. in the presence of BF_3 catalyst. The resultant ester had a Ring and Ball melting point of 270°F. and an acid No. of 77.

In a similar manner terpene-phenol condensates are prepared from β -pinene dipentene, terpinene, limonene, and terpenolene by reaction with phenol, cresol, chlorophenol and resorcinol. The resin esters of these condensates are likewise prepared in a similar manner by reaction with tall oil rosin, gum rosin, and wood rosin.

WHAT WE CLAIM IS:—

1. An adhesive composition comprising a chloroprene polymer as hereinbefore defined, a rosin ester of a terpene-phenol condensate, a polyvalent metal oxide, and a solvent for said chloroprene polymer.
2. A composition as claimed in claim 1 wherein the rosin ester of the terpene-phenol condensate is derived from a phenol having at least one active ortho or para position on the benzene ring.
3. A composition as claimed in claim 2, wherein the phenol is hydroxybenzene cresol, xylenol, chlorophenol, dichlorophenol, nitrophenol, catechol, resorcinol, hydroquinone, bis(*p*-hydroxyphenyl)methane, bis(*p*-hydroxyphenyl)ethane, or 2,2-bis(*p*-hydroxyphenyl)propane.
4. A composition as claimed in any one of the preceding claims wherein the rosin ester of the terpen-phenol condensate is derived from a terpene hydrocarbon having the general formula $C_{10}H_{16}$, or a terpene alcohol.
5. A composition as claimed in claim 4 wherein the terpene is α -pinene, β -pinene, dipentene, terpinene, limonene, 7-methyl-3-methylene-1,6-octadiene, or terpenolene.
6. A composition as claimed in any one of the preceding claims wherein the rosin ester of the terpen-phenol condensate is derived from gum rosin, wood rosin, or tall oil rosin.
7. A composition as claimed in any one of the preceding claims wherein said rosin ester is a tall oil rosin ester of the α -pinene condensate of phenol.
8. A composition as claimed in any one of the preceding claims wherein the rosin ester is present in an amount of from 5 to 200 parts by weight per 100 parts by weight chloroprene polymer.
9. A composition as claimed in claim 8 wherein the rosin ester is present in an amount of from 25 to 75 parts by weight per 100 parts by weight chloroprene polymer.
10. A composition as claimed in any one of the preceding claims wherein the solvent is an aromatic hydrocarbon, an aliphatic ketone, a chlorinated aliphatic hydrocarbon, or a lower aliphatic ester.
11. A composition as claimed in claim 10 wherein the solvent is benzene, toluene, xylene, acetone, methyl ethyl ketone, trichloroethylene, or ethyl acetate.
12. A composition as claimed in any one of the preceding claims wherein the polyvalent metal oxide is an oxide of a group II polyvalent metal.
13. A composition as claimed in claim 12 wherein the polyvalent metal oxide is magnesium oxide.
14. A composition as claimed in claim 12 wherein the polyvalent metal oxide is zinc oxide.
15. A composition as claimed in claim 12 wherein said polyvalent metal oxide is a mixture of magnesium oxide and zinc oxide.
16. A composition as claimed in any one of the preceding claims wherein the polyvalent metal oxide is present in an amount of from 1 to 32 parts by weight per 100 parts by weight chloroprene polymer.
17. A composition as claimed in any one of the preceding claims which further comprises an addition compound derived from maleic or fumaric acid or maleic anhydride and the rosin ester of the terpene-phenol condensate.
18. A composition as claimed in claim 17 wherein the addition compound is present in an amount of from 0 to 32 parts by weight per 100 parts by weight rosin.
19. A composition as claimed in any one of the preceding claims wherein said chloroprene polymer is chloroprene homopolymer.
20. A composition as claimed in any one of claims 1 to 18 wherein the chloroprene polymer is a chloroprene copolymer substantially as hereinbefore described.
21. An adhesive composition substantially as described herein with reference to the Example.
22. A method of imparting enhanced tack range to chloroprene adhesive compositions by incorporating therewith a rosin ester of a terpene-phenol condensate, a polyvalent metal oxide, and a solvent for said chloroprene polymer.
23. A method as claimed in claim 22 wherein said rosin ester is a tall oil rosin ester.
24. A method as claimed in claim 22 or claim 23 wherein said terpene-phenol condensate is an α -pinene condensate of phenol.
25. A method of adhering articles which method comprises the use of an adhesive composition as claimed in any one of claims 1 to 21.
26. An article when prepared by a method as claimed in claim 25.

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